(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 353 981 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of patent specification: **11.01.95**

(51) Int. Cl.[6]: **C08L 23/10**, //(C08L23/10, 23:14)

(21) Application number: **89307780.0**

(22) Date of filing: **31.07.89**

(54) Polypropylene resin composition.

(30) Priority: **04.08.88 JP 195058/88**

(43) Date of publication of application:
07.02.90 Bulletin 90/06

(45) Publication of the grant of the patent:
11.01.95 Bulletin 95/02

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

(56) References cited:
EP-A- 0 015 066
EP-A- 0 144 642
EP-A- 0 168 129
EP-A- 0 198 981
EP-A- 0 228 543
EP-A- 0 294 770
US-A- 4 113 806

(73) Proprietor: **MITSUI PETROCHEMICAL INDUSTRIES, LTD.**
2-5, Kasumigaseki 3-chome
Chiyoda-ku
Tokyo 100 (JP)

(72) Inventor: **Tanaka, Mutsuhiro Mitsui Petr. Industries, Ltd.**
3, Chigusakaigan
Ichihara-shi
Chiba (JP)
Inventor: **Sugi, Masahiro Mitsui Petr. Industries, Ltd.**
3, Chigusakaigan
Ichihara-shi
Chiba (JP)

(74) Representative: **Myerscough, Philip Boyd et al**
J.A.KEMP & CO.
14, South Square
Gray's Inn
London WC1R 5LX (GB)

EP 0 353 981 B1

Description

The present invention relates to a polypropylene resin composition having an excellent heat seal strength, low temperature impact resistance and transparency, when used, for example, as a film.

Polypropylene resins have excellent rigidity and heat resistance, but have the drawback of a low impact strength, particularly a low impact resistance at low temperatures. To eliminate this drawback, it is well known in the art that a rubber component comprising an ethylenic random copolymer such as ethylene-propylene random copolymer or ethylene-butene random copolymer can be mixed with a polypropylene resin.

In the above-mentioned polypropylene resin of the prior art, however, since the size of the dispersed particles of the rubber component such as ethylene-propylene random copolymer or ethylene-butene random copolymer is large, the heat seal strength cannot be enhanced, i.e. it is generally difficult to obtain a composition having a good balance between the heat seal strength and the low temperature impact resistance, and the transparency is poor. For example, a heat-sealable polypropylene film comprising a low-crystallinity α-olefin copolymer is known from EP-A- 144 642.

Accordingly, the present invention seeks to eliminate the above-mentioned disadvantages of the prior art and to provide a polypropylene resin composition having an improved heat seal strength and having an excellent low temperature impact resistance and transparency, by reducing the size of the dispersed particles of the rubber component in the resin composition.

In accordance with the present invention, there is provided a propylene resin composition comprising:

(A) 50% to 99% by weight of a polypropylene resin, and

(B) 1% to 50% by weight of a rubber component,

the rubber component (B) comprising a random copolymer composition containing:

(i) an ethylenic random copolymer selected from the group consisting of random copolymers of ethylene with an α-olefin having 3 to 20 carbon atoms having an ethylene content of 60 to 95 mol%, a crystallinity of 40% or less and an $MFR_{230°C}$ of 0.1 to 50 g/10 min. and

(ii) a propylenic random copolymer selected from the group consisting of random copolymers of propylene with an α-olefin having 2 to 20 carbon atoms except for propylene having a propylene content of 60 to 95 mol% and a $MFR_{230°C}$ of 0.1 to 50 g/10 min.,

at a weight ratio of (i):(ii) of from 95:5 to 20:80.

The polypropylene resins usable as the component (A) in the present invention include homopolymers of propylene, or random or block copolymers of propylene with other α-olefins having 2 and 4 to 20 carbon atoms, such as ethylene or 1-butene, generally containing 90 mol% or more of propylene units and having an insoluble matter in boiling n-heptane of 90% or more, preferably 93% or more.

The polypropylene resin (A) can be typically prepared by using a catalyst formed from a solid titanium catalyst component and an organometallic compound component, or a catalyst formed from both of these components and an electron donor.

Examples of the solid titanium catalyst components are titanium trichloride or titanium tetrachloride compositions prepared by various methods, or carried titanium catalyst components comprising magnesium, a halogen, an electron donor, preferably an aromatic carboxylic acid or an alkyl-containing ether and titanium as the essential components, preferably having a specific surface area of 100 m^2/g or more. Particularly, those components prepared by using the latter carried catalyst components are preferable.

As the organometallic compound component, organic aluminum compounds are preferably used. Examples of such compounds are trialkylaluminum, dialkylaluminum halide, alkylaluminum sesquihalide and alkylaluminum dihalide. The preferable organic aluminum compounds depend upon the kind of titanium catalyst component. Preferable examples of the electron donors are organic compounds containing, for example, nitrogen, sulfur, oxygen, silicon, and boron, such as esters or ethers.

The preparations of the above-mentioned polypropylenes by using carried catalyst components are disclosed, for example, in Japanese Unexamined Patent Publication (Kokai) Nos. 50-108385, 50-126590, 51-20297, 51-28189, and 52-151691.

The ethylenic random copolymer (i) constituting the rubber component of the component (B) include random copolymers composed mainly of ethylene with other α-olefins having 3 to 20 carbon atoms. The ethylene-α-olefin copolymer usable in the present invention may have an ethylene content of 60 to 95 mol%, preferably 70 to 90 mol%, a $MFR_{230°C}$ (melt index according to ASTM D 1238, 65T, 230 °C) of 0.1 to 50 g/min., preferably 0.1 to 20 g/min., a crystallinity of 40% or less, preferably 20% or less, with α-olefin having 3 to 20, preferably 3 to 10, more preferably 3 to 5 carbon atoms. These ethylenic random copolymers (i) can be used alone or as any mixture thereof.

When the ethylene content is less than 60 mol%, the resin becomes difficult to handle because, for example, of blocking. But when the ethylene content exceeds 95 mol%, a satisfactory low temperature impact resistance cannot be obtained. When $MFR_{230°C}$ is outside the above range, dispersibility into the polypropylene will become difficult, and when the crystallinity exceeds 40%, a material having a satisfactory impact resistance improving effect cannot be obtained. Also, when the number of carbon atoms exceeds 20, the rubbery properties of the polymer are reduced, and therefore, the effect thereof as an impact resistance improving material is unpreferably lost.

The propylenic random copolymers (ii) are random copolymer rubbers mainly composed of propylene with other α-olefins having 2 to 20 carbon atoms except for propylene. The propylene-α-olefin copolymers usable in the present invention have a propylene content of 60 to 95 mol%, preferably 70 to 90 mol%, a $MFR_{230°C}$ (melt index according to ASTM D 1238, 65T, 230°C) of 0.1 to 50 g/min., preferably 0.1 to 20 g/min., a crystallinity of 40% or less, preferably 20% or less, with α-olefin having 2 to 20, preferably 2 to 10, more preferably 2 to 5 carbon atoms. These propylenic random copolymers (ii) may be used alone or as any mixture thereof.

The ethylenic random copolymers (i) can be prepared by randomly polymerizing a plurality of monomers by using a catalyst system comprising a soluble vanadium compound and an alkylaluminum halide compound.

Examples of the soluble vanadium compound to be used as the catalyst for polymerization include vanadium tetrachloride, vanadium oxytrichloride, vanadium triacetylacetonate and oxyvanadium triacetylacetonate. Examples of the alkylaluminum halide compound which is combined with the soluble vanadium compound to constitute the catalyst for polymerization include ethylaluminum dichloride, diethylaluminum monochloride, ethylaluminum sesquichloride, diethylaluminum monobromide, diisobutylaluminum monochloride, isobutylaluminum dichloride and isobutylaluminum sesquichloride.

The polymerization can be carried out in a solution or suspension, or in an intermediate region therebetween, and in all cases an inert solvent is preferably used as the reaction medium. The inert solvents usable for the polymerization include aliphatic hydrocarbons having about 3 to 12 carbon atoms, including propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, kerosene, or halogenated hydrocarbons such as methyl chloride, ethyl chloride, ethylene dichloride, which may be used alone or as any mixture thereof. The polymerization temperature may be generally 0 to 100°C.

The propylenic random copolymers (ii) can be prepared by randomly polymerizing a plurality of monomers by using a catalyst similar to that for the above polypropylene resin (A) and by a similar procedure.

The rubber component (B) of the present invention comprises a random copolymer composition comprising the above-mentioned ethylenic random copolymer (i) and the above-mentioned propylenic random copolymer (ii) formulated to a weight ratio (i):(ii) of 95:5 to 20:80, preferably 70:30 to 30:70.

The polypropylene resin composition of the present invention comprises 50 to 99% by weight, preferably 70 to 90% by weight, of the above-mentioned polypropylene resin (A) and 1 to 50% by weight, preferably 10 to 30% by weight of the above-mentioned rubber component (B).

In the polypropylene resin composition of the present invention, other resin components, such as polyethylene resin, can be formulated within the range which will not hinder the obtaining of the object of the present invention, and further, various additives can be formulated, such as an antioxidant, UV-ray absorber, lubricant, nucleating agent, antistatic agent, flame retardant, pigment, dye, and inorganic or organic fillers.

For the preparation of the polypropylene resin composition of the present invention, any known methods may be employed either alone or in combination, such as the method whereby the respective components are mixed by a mixing machine such as a V-type blender, ribbon blender, or Henschel mixer, or the method in which the components are kneaded by a kneading machine such as an extruder, mixing rolls, Banbury mixer, or kneader.

The polypropylene resin composition thus obtained, wherein a propylenic random copolymer exists as the rubber component, has a good dispersibility of the ethylenic random copolymer in the polypropylene resin, whereby the dispersed particle size is reduced to give a molded product such as a film having an improved heat seal strength and an excellent low temperature impact resistance and transparency.

The polypropylene resin composition of the present invention is suitable for the preparation of, for example, films and sheets for which a heat sealability, low temperature resistance and transparency are required, such as films for packaging, but can be also utilized for other molded products.

As described above, since the polypropylene resin composition of the present invention contains rubber components comprising an ethylenic random copolymer and a propylenic random copolymer, the heat

sealability can be improved and a molded product having an excellent low temperature impact resistance and transparency can be obtained.

EXAMPLES

The present invention will now be further illustrated in detail by the following Examples, wherein "parts" are all by weight and "%" is mol%, unless otherwise noted.

Example 1

An 85 parts amount of a polypropylene resin with an ethylene content of 2.3%, a $MFR_{230°C}$ of 6.5 g/10 min., and a melting point (Tm) of 141 °C, 5 parts of an ethylenepropylene random copolymer having an ethylene content of 81%, a $MFR_{230°C}$ of 5.4 g/10 min., and 10 parts of a propylene-butene random copolymer having a propylene content of 81%, a $MFR_{230°C}$ of 6.0 g/10 min., and a Tm of 110 °C were mixed in a Henschel mixer. The mixture was pelletized and then molded to obtain a film having a thickness of 60 μm. Next, the film impact at 0 °C, haze, gloss and heat seal characteristics for the film obtained were measured. The film impact was measured by a pendulum-type film impact measuring device, and the heat seal characteristics were measured for the respective characteristics for the heat seal initiation temperature (H.S. initiation temperature) at which a strength of 0.5 kg/15 mm is exhibited when the film is heat sealed under a pressure of 2 kg/cm^2 for one second and subjected to T-peeling at 300 mm/min and heat seal strength at 150 °C (H.S. strength).

The results are shown in Table 1.

Examples 2 - 12 and Comparative Examples 1 - 5

Films obtained from the compositions shown in Table 1 were molded and measured in the same manner as in Example 1. The results are shown in Table 1.

Table 1

Composition		Example 1	2	3	4	5	6	7	8	9	10	11	12	Comparative Example 1	2	3	4	5
Random PP	1)	85	85	85	85	85	85	80	80	80	85	85	85	100	85	85	85	80
EPR	2)	5	7.5	10	-	-	-	-	-	-	5	7.5	10	-	15	-	-	-
EBR	3)	-	-	-	5	7.5	10	6.7	10	13.3	-	-	-	-	-	15	-	20
PBR	4)	10	7.5	5	10	7.5	5	13.3	10	6.7	-	-	-	-	-	-	15	-
PER	5)	-	-	-	-	-	-	-	-	-	10	7.5	5	-	-	-	-	-
Film impact (at 0°C)		1700	2400	2400	1700	2000	1700	1600	2100	1800	1900	2300	2400	650	1900	1900	720	2000
Haze (%)		0.8	0.9	0.9	0.8	0.8	1.0	0.7	1.0	2.2	0.8	0.8	0.9	0.9	2.4	4.6	0.9	8.8
Gloss (%)		133	130	131	132	132	121	132	121	86	130	129	127	132	85	57	133	36
H.S. initiation temp. (°C)		132	132	131	135	133	132	130	128	126	130	131	131	139	130	131	137	125
H.S. strength (at 150°C)		2.2	2.1	2.0	2.1	2.1	1.9	1.9	1.8	1.5	2.1	2.1	2.1	2.4	0.75	0.74	2.21	0.6

1) Polypropylene resin — Ethylene content 2.3%, $MFR_{230°C}$ 6.5 g/10 min. Tm = 141°C

2) Ethylene-propylene random copolymer — Ethylene content 81%, $MFR_{230°C}$ 5.4 g/10 min. Tm = --

3) Ethylene-butene random copolymer — Ethylene content 80%, $MFR_{230°C}$ 6.7 g/10 min. Tm = --

4) Propylene-butene random copolymer — Propylene content 81%, $MFR_{230°C}$ 6.0 g/10 min. Tm = 110°C

5) Propylene-ethylene random copolymer — Propylene content 70%, $MFR_{230°C}$ 2.5 g/10 min. Tm = --

Claims

1. A propylene resin composition comprising:
   (A) 50% to 99% by weight of a polypropylene resin and

(B) 1% to 50% by weight of a rubber component, said rubber component (B) comprising a random copolymer composition containing:

(i) an ethylenic random copolymer selected from the group consisting of random copolymers of ethylene with an α-olefin having 3 to 20 carbon atoms having an ethylene content of 60 to 95 mol% a crystallinity of 40% or less and an $MFR_{230°C}$ of 0.1 to 50 g/10 min. and

(ii) a propylenic random copolymer selected from the group consisting of random copolymers of propylene with an α-olefin having 2 to 20 carbon atoms, except for propylene, having a propylene content of 60 to 95 mol% and a $MFR_{230°C}$ of 0.1 to 50 g/10 min.,

at a weight ratio of (i):(ii) of from 95:5 to 20:80.

2. A composition according to claim 1, wherein the polypropylene resin (A) is at least one propylene homopolymer or random or block copolymer of propylene with an α-olefin having 2 or 4 to 20 carbon atoms having a propylene content of at least 90 mol%.

3. A composition according to claim 1 or 2, wherein the weight ratio (i):(ii) in rubber component (B) is 70:30 to 30:70.

4. A composition according to claim 1, 2 or 3 wherein the ethylenic random copolymer (i) is composed of 60 to 95 mol% of ethylene and the remainder of at least one α-olefin with 3 to 20 carbon atoms.

5. A composition according to any one of claims 1 to 4 wherein the propylenic random copolymer (ii) is composed of 60 to 95 mol% of propylene and the remainder of at least one α-olefin having 2 or 4 to 20 carbon atoms.

6. Shaped articles, such as films, of a composition as claimed in any one of the preceding claims.

Patentansprüche

1. Propenharzzusammensetzung, welche umfaßt:

(A) 50 bis 99 Gew.-% eines Polypropenharzes und

(B) 1 bis 50 Gew.-% einer Kautschukkomponente, wobei die Kautschukkomponente (B) eine Zufallscopolymerzusammensetzung umfaßt, welche enthält:

(i) ein Ethen-Zufallscopolymer, ausgewählt aus der aus Zufallscopolymeren von Ethen mit einem α-Olefin mit 3 bis 20 Kohlenstoffatomen bestehenden Gruppe, mit einem Ethengehalt von 60 bis 95 Mol.-% und einem Schmelzflußindex $MFR_{230°C}$ von 0,1 bis 50 g/10 min und

(ii) einem Propen-Zufallscopolymer, ausgewählt aus der aus Zufallscopolymeren von Propen mit einem α-Olefin mit 2 bis 20 Kohlenstoffatomen bestehenden Gruppe außer Propen, mit einem Propengehalt von 60 bis 95 Mol.-% und einem Schmelzflußindex $MFR_{230°C}$ von 0,1 bis 50 g/10 min,

mit einem Gewichtsverhältnis von (i):(ii) von 95:5 bis 20:80.

2. Zusammensetzung nach Anspruch 1, worin das Polypropenharz (A) wenigstens ein Propenhomopolymer oder Zufalls- oder Blockpolymer aus Propen mit einem α-Olefin mit 2 oder 4 bis 20 Kohlenstoffatomen mit einem Propengehalt von mindestens 90 Mol.-% ist.

3. Zusammensetzung nach Anspruch 1 oder 2, worin das Gewichtsverhältnis (i):(ii) in der Kautschukkomponente (B) 70:30 bis 30:70 beträgt.

4. Zusammensetzung nach Anspruch 1, 2 oder 3, worin das Ethen-Zufallscopolymer (i) aus 60 bis 95 Mol.-% Ethen und der Rest aus wenigstens einem α-Olefin mit 3 bis 20 Kohlenstoffatomen zusammengesetzt ist.

5. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin das Propen-Zufallscopolymer (ii) aus 60 bis 95 Mol.-% Propen und der Rest aus wenigstens einem α-Olefin mit 2 oder 4 bis 20 Kohlenstoffatomen zusammengesetzt ist.

6. Geformte Gegenstände, wie beispielsweise Filme, aus einer Zusammensetzung nach einem der vorangegangenen Ansprüche.

Revendications

1. Composition de résine propylénique comprenant:
   (A) de 50% à 99% en poids d'une résine polypropylénique, et
   (B) de 1% à 50% en poids d'un composant de caoutchouc, ledit composant de caoutchouc (B) comprenant une composition de copolymère au hasard contenant:
      (i) un copolymère au hasard éthylénique choisi parmi le groupe composé de copolymères au hasard d'éthylène avec une α-oléfine ayant de 3 à 20 atomes de carbone, ayant une teneur en éthylène de 60 à 95% mol., une cristallinité de 40% ou moins et un $MFR_{230°C}$ de 0,1 à 50 g/10 min., et
      (ii) un copolymère au hasard propylénique choisi parmi le groupe composé de copolymères au hasard de propylène avec une α-oléfine ayant de 2 à 20 atomes de carbone, sauf pour le propylène, ayant une teneur en propylène de 60 à 95% mol. et un $MFR_{230°C}$ de 0,1 à 50 g/10 min..
   suivant un rapport en poids de (i):(ii) de 95:5 à 20:80.

2. Composition suivant la revendication 1, dans laquelle la résine polypropylénique (A) est au moins un homopolymère de propylène ou copolymère au hasard ou en masse de propylène avec une α-oléfine ayant 2 ou de 4 à 20 atomes de carbone, ayant une teneur en propylène d'au moinst 90% mol.

3. Composition suivant la revendication 1 ou 2, dans laquelle le rapport en poids (i):(ii) dans le composant caoutchouc (B) est de 70:30 à 30:70.

4. Composition suivant la revendication 1, 2 ou 3, dans laquelle le copolymère au hasard éthylénique (i) est composé de 60 à 95% mol. d'éthylène et pour le reste d'au moins une α-oléfine avec de 3 à 20 atomes de carbone.

5. Composition suivant l'une ou l'autre des revendications 1 à 4, dans laquelle le copolymère au hasard propylénique (ii) est composé de 60 à 95% mol. de propylène et pour le reste d'au moins une α-oléfine ayant 2 ou de 4 à 20 atomes de carbone.

6. Articles façonnés, tels que films, d'une composition suivant l'une ou l'autre des revendications précédentes.